THE ELECTRODEPOSITION OF CHROMIUM

BY

ROBERT WALTER PARRY

B. S., Utah State Agricultural College, 1940
M. S., Cornell University, 1942

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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THE ELECTRODEPOSITION OF CHROMIUM

I. Introduction

Bright, hard chromium plates are produced commercially by electrodeposition from a bath composed of an aqueous solution of chromic acid and a small amount of a foreign anion catalyst. The most commonly used bath is 2 to 4 molar in chromic acid and contains sulfate as the catalyst in a concentration such that the molar ratio of chromate to sulfate is about 100 to 1 ($CrO_3/SO_4^{=} = 100/1$). By accurate control of plating conditions deposits of high quality can be produced.

Though widely used this process has a number of limitations. 1) Current efficiency of the cathode reaction is low, running around 5-20% under favorable conditions. 2) Chromium plated at the cathode can not be replaced by anode corrosion, but must be replaced by addition of chromic acid to the solution. This requires careful control of bath composition. 3) Throwing power of the solution is poor. 4) All variables must be carefully controlled within narrow limits to obtain satisfactory plates. 5) The chromium deposited is porous; this condition necessitates application of a protective undercoat of copper and/or nickel if corrosion resistance is to be obtained in the finished product. These difficulties are of sufficient economic importance to justify further investigation of chromium plating. In addition, the theory of the deposition process is inadequate and merits further study.

II. Deposition from Di- and Trivalent Chromium Salts

A review of the literature on the deposition of chromium from solutions of the di- and trivalent salts reveals that observations of previous workers do not agree in many cases. Cases of conflicting data were investigated. Five types of

plating cells were used; two contained diaphragms to separate the anolyte and catholyte. Cathodes were of copper. Data from the literature together with data obtained in this work support the early hypothesis of Carveth and Mott (1) that chromous ion is important in the deposition process. This was particularly apparent in a comparison of deposition from chromic and chromous chlorides. Satisfactory deposits of chromium were obtained from chromous chloride but not from chromic chloride solutions. Both Chromic and chromous sulfate solutions yielded plates. It is possible that sulfate ion may aid in stabilizing the chromous ion in the region immediately adjacent to the cathode.

The efficiency of a chromic sulfate bath was reduced by boiling; after prolonged boiling, no plate could be obtained from this bath. Such a phenomenon is probably due to the formation by olation of large complex chromic sulfate ions. Allowing a piece of copper to stand in contact with a chromic sulfate plating bath before passage of the electric current prevented the deposition of chromium from the bath. This observation had been reported previously by Kasper (2). These points are of interest in reconciling conflicting data in the literature. Dony-Henault (3) advanced the theory that plating from chromic sulfate or chloride solutions can take place only from the violet isomer, $[Cr(H_2O)_6]^{+++}$, not the green isomers, $[Cr(H_2O)_5Cl]^{++}$ and $[Cr(H_2O)_4Cl_2]^{+}$. His theory was not supported by the results of this investigation. No significant difference in platting behavior was observed between the green and violet isomers of chromic chloride.

No plates were obtained from solutions of the following complex ions of chromium: 1) $[Cr(\text{ethylenediamine})_3]^{+++}$, 2) $K_3[Cr(\text{oxalate})_3]$, 3) $[Cr(\text{urea})_6]^{+++}$, 4) $[Cr(NH_3)_5Cl]^{++}$, 5) $[Cr(NH_3)_6]^{+++}$. No complex ion of divalent chromium was found which was stable in a solution exposed to air.

The E_o value for the chromous-chromium couple was estimated from the decomposition potential of a one molar chromous sulfate solution. A value of $0.83 \pm .03$ volts was

obtained which is in good agreement with the value 0.86 calculated by Latimer (7) from thermal data.

III. Deposition of Chromium from the Hexavalent State

Pure chromic acid can not be reduced electrolytically at a solid metal cathode. The presence of small amounts of certain foreign anions such as chloride, sulfate, nitrate, or fluoborate makes reduction possible. According to the most commonly accepted theory this behavior is due to the formation of an insoluble film of chromic chromate or chromic oxide over the surface of the cathode. The film is impermeable to large polychromate ions but permeable to small hydrogen ions. Sulfate or other foreign anions supposedly dissolve this film or make it permeable to chromate. No satisfactory explanation has yet been advanced for the action of a foreign anion in dissolving this film. Mechanisms suggested by Kaspar (4) and by Müller (5) postulate directly or indirectly the formation of cationic coordination compounds from trivalent chromium and the foreign anion. The ability of non coordinating anions such as nitrate and fluoborate to act as catalysts makes these mechanisms unacceptable.

The reduction process in the presence of different foreign anion catalysts was followed by means of current-voltage curves. It was found that the ability of an anion to catalyze the reduction of chromic acid to trivalent chromium is not necessarily related to the ability of the anion to promote reduction to the metal. The ability of several anions to promote reduction to trivalent chromium falls in the order 1) chloride, 2) sulfate, 3) fluoborate, 4) nitrate. Perchlorate had a scarcely detectable catalytic effect, and phosphate and acetate were absolutely ineffective as catalysts. Sulfate was the most effective catalyst in promoting reduction to the metal. Nitrate, perchlorate, phosphate, and acetate did not promote the deposition of metal at all.

Current-voltage curves were obtained in a special electrolysis cell containing a sintered glass diaphragm to separate

catholyte and anolyte, an electric stirrer to stir the catholyte, and a circular copper cathode placed on the bottom of the cell. An atmosphere of nitrogen was maintained above the catholyte. One tenth to 0.25 molar solutions of chromic acid in 2 N solutions of a supporting electrolyte, such as hydrochloric, sulfuric, perchloric, and phosphoric acids, were electrolyzed in the above cell. Current-voltage curves for the reduction in hydrochloric, perchloric, and sulfuric acids were very similar to typical polarographic diffusion curves. When phosphoric acid was the supporting electrolyte, a broken, irregular curve was obtained which did not resemble a diffusion curve.

IV. Correlation of the Plating Behavior from Different Valence States

By putting the electrodeposition process through a thermochemical cycle similar to the Born-Haber cylcle it was found that the reduction of chromic ions is retarded by the large amount of energy needed to strip the water of hydration from the trivalent chromium ion ($\triangle H = 1320$ kcal) (6). It can be shown from energy considerations that the most probable way for a chromate ion to break is to give a Cr^{++} and 4 O^{-} ions. The $\triangle H$ value for this process is 957 kcal. A similar thermochemical treatment of the chromous ion shows that 672 kcal are needed to remove the water of hydration from the divalent ion. Since these values are, in a sense, "pseudo activation energies" for the electrodeposition process, the relative ease of plating from the three valence states should be chromous salts, chromic acid, chromic salts. Current efficiency data indicate that this is actually the observed order. E_o values would predict the order: chromic acid, chromic salts, and chromous salts, but the E_o values consider only equilibrium energy states and no energy barriers in the process.

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VITA

The author was born in Ogden, Utah, on October 1, 1917. He received his elementary education in the Ogden Public Schools and graduated from Ogden High School in 1934. From 1934 to 1936 he attended Weber Junior College in Ogden, Utah, and finished his college work at the Utah State Agricultural College in Logan, Utah, receiving the degree of Bachelor of Science with a major in soil chemistry in 1940. From the fall of 1940 to July of 1942 he held a teaching and research assistantship in the Department of Agronomy and Soils at Cornell University, receiving the degree of Master of Science in 1942. After spending six months in the explosives industry, he came to the University of Illinois in January of 1943 as a special research assistant on a National Defense Research Committee contract. He was thus employed until February, 1946. He entered the graduate school of the University of Illinois in February, 1943. From February, 1946, to June, 1946, he was a teaching assistant in chemistry and at the present time is a University Fellow in Chemistry.